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Date: August 4, 2004 Name: G. Peter Nichols

Signature:

BRINKS
HOFFER
GILSON
& LIONE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Appln. of: Schaekers et al.Appln. No.: 10/733,907Filed: December 11, 2003For: SOLVENT EXTRACTION MIXTURE FOR
THE SEPARATION OF GROUPS OF
BASE METALSAttorney Docket No: 10908/6

Examiner: not yet assigned

Art Unit: 1754

Commissioner for Patents
P. O. Box 1450
Alexandria, VA 22313-1450

TRANSMITTAL

Sir:

Attached is/are:

- ☒ Submission of Certified Copy of Priority Documents; Priority Documents (2); and
☒ Return Receipt Postcard

Fee calculation:

- ☒ No additional fee is required.
☐ Small Entity.
☐ An extension fee in an amount of \$_____ for a _____-month extension of time under 37 C.F.R. § 1.136(a).
☐ A petition or processing fee in an amount of \$_____ under 37 C.F.R. § 1.17(____).
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					Small Entity			Not a Small Entity	
	Claims Remaining After Amendment		Highest No. Previously Paid For	Present Extra	Rate	Add'l Fee	or	Rate	Add'l Fee
Total		Minus			x \$9=			x \$18=	
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First Presentation of Multiple Dep. Claim					+\$145=			+\$290=	
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☐ Please charge Deposit Account No. 23-1925 in the amount of \$_____. A copy of this Transmittal is enclosed for this purpose.
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☒ The Director is hereby authorized to charge payment of any additional filing fees required under 37 CFR § 1.16 and any patent application processing fees under 37 CFR § 1.17 associated with this paper (including any extension fee required to ensure that this paper is timely filed), or to credit any overpayment, to Deposit Account No. 23-1925.

Respectfully submitted,

G. Peter Nichols (Reg. No. 34,401)

August 4, 2004

Date

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Date of Deposit: August 4, 2004

G. Peter Nichols, Reg. No. 34,401

Name of Applicant, Assignee or
Registered Representative

Signature

Our File No. 10908/6

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:)
Schaekers et al.)
Serial No. 10/733,907)
Filing Date: December 11, 2003)
For SOLVENT EXTRACTION MIXTURE)
FOR THE SEPARATION OF)
GROUPS OF BASE METALS)

SUBMISSION OF CERTIFIED COPY OF PRIORITY DOCUMENTS

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

Transmitted herewith is a certified copy of the following priority documents for the above-named U.S. application:

1. PCT Application No. PCT/ZA02/00096 filed June 5, 2002
2. South African Provisional Patent Application No. 2001/4794 filed June 13, 2001.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "G. Peter Nichols".

G. Peter Nichols
Registration No. 34,401
Attorney for Applicants

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Sertifikaat

REPUBLIEK VAN SUID AFRIKA

PATENT KANTOOR
DEPARTEMENT VAN HANDEL
EN NYWERHEID



Certificate

REPUBLIC OF SOUTH AFRICA

PATENT OFFICE
DEPARTMENT OF TRADE AND
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Hiermee word gesertifiseer dat
This is to certify that

the documents annexed hereto are true copies of:

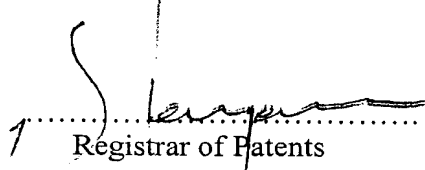
PCT Application No. PCT/ZA02/00096 as originally filed with the South African Receiving Office on 05 June 2002 in the name of BILLITON SA LIMITED for an invention entitled: " SOLVENT EXTRACTION MIXTURE FOR THE SEPARATION OF GROUPS OF BASE METALS."

**CERTIFIED COPY OF
PRIORITY DOCUMENT**

Geteken te
Signed at **PRETORIA**

in die Republiek van Suid-Afrika, hierdie
in the Republic of South Africa, this

dag van
day of **30th June 2004**


Registrar of Patents

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1/4

INT1056/MAJR

PCT REQUEST

Original (for SUBMISSION) - printed on 04.06.2002 05:41:35 PM

0	For receiving Office use only	
0-1	International Application No.	PET/ZA02 / 00096
0-2	International Filing Date	05 JUN 2002
0-3	Name of receiving Office and "PCT International Application"	SAPTO
0-4	Form - PCT/RO/101 PCT Request	
0-4-1	Prepared using	PCT-EASY Version 2.92 (updated 01.01.2002)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	South African Patents and Trade Marks Office (RO/ZA)
0-7	Applicant's or agent's file reference	INT1056/MAJR
I	Title of invention	SOLVENT EXTRACTION MIXTURE FOR THE SEPARATION OF GROUPS OF BASE METALS
II	Applicant	
II-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
II-4	Name	BILLITON SA LIMITED
II-5	Address:	200 Hans Strijdom Drive 2194 Randburg South Africa
II-6	State of nationality	ZA
II-7	State of residence	ZA
II-8	Telephone No.	+27 11 792-7090
II-9	Facsimile No.	+27 11 792-7097
III-1	Applicant and/or inventor	
III-1-1	This person is:	applicant and inventor
III-1-2	Applicant for	US only
III-1-4	Name (LAST, First)	SCHAEKERS, Jozef, Marie
III-1-5	Address:	c/o 200 Hans Strijdom Drive 2194 Randburg South Africa
III-1-6	State of nationality	ZA
III-1-7	State of residence	ZA

REGISTRAR OF PATENTS DESIGNS,
TRADE MARKS AND COPYRIGHT

2002 -06- 06

REGISTRATEUR VAN PATENTE, MODELLE,
HANDELSMERKE EN OUTEURSREG

PCT REQUEST

INT1056/MAJR

Original (for SUBMISSION) - printed on 04.06.2002 05:41:35 PM

III-2	Applicant and/or inventor	
III-2-1	This person is:	applicant and inventor
III-2-2	Applicant for	US only
III-2-4	Name (LAST, First)	DU PREEZ, Jan, Gysbert, Hermanus
III-2-5	Address:	c/o University of Port Elizabeth 6000 Port Elizabeth South Africa
III-2-6	State of nationality	ZA
III-2-7	State of residence	ZA
IV-1	Agent or common representative; or address for correspondence The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
IV-1-1	Name	MCCALLUM RADEMEYER & FREIMOND
IV-1-2	Address:	P O Box 1130, 7 Maclyn House, Bordeaux 2125 Randburg South Africa
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IV-1-4	Facsimile No.	+27 11 787-4516
IV-1-5	e-mail	mcrafr@iafrica.com
IV-2	Additional agent(s)	additional agent(s) with same address as first named agent
IV-2-1	Name(s)	RADEMEYER, Montague, Ampie, John
V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AP: GH GM KE LS MW MZ SD SL SZ TZ UG ZM ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE TR and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GQ GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT

PCT REQUEST

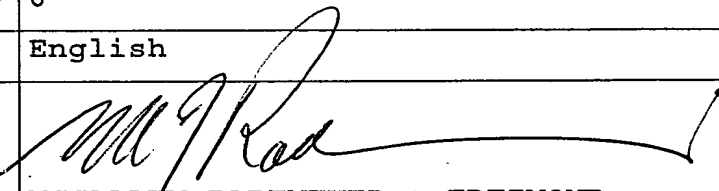
INT1056/MAJR

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V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH&LI CN CO CR CU CZ DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ OM PH PL PT RO RU SD SE SG SI SK SL TJ TM TN TR TT TZ UA UG US UZ VN YU ZA ZM ZW	
V-5	Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.		
V-6	Exclusion(s) from precautionary designations	NONE	
VI-1	Priority claim of earlier national application		
VI-1-1	Filing date	13 June 2001 (13.06.2001)	
VI-1-2	Number	2001/4794	
VI-1-3	Country	ZA	
VI-2	Priority document request The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) identified above as item(s):	VI-1	
VII-1	International Searching Authority Chosen	European Patent Office (EPO) (ISA/EP)	
VIII	Declarations	Number of declarations	
VIII-1	Declaration as to the identity of the inventor	-	
VIII-2	Declaration as to the applicant's entitlement, as at the international filing date, to apply for and be granted a patent	-	
VIII-3	Declaration as to the applicant's entitlement, as at the international filing date, to claim the priority of the earlier application	-	
VIII-4	Declaration of inventorship (only for the purposes of the designation of the United States of America)	-	
VIII-5	Declaration as to non-prejudicial disclosures or exceptions to lack of novelty	-	

PCT REQUEST

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IX	Check list	number of sheets	electronic file(s) attached
IX-1	Request (including declaration sheets)	4	-
IX-2	Description	15	-
IX-3	Claims	2	-
IX-4	Abstract	1	EZABST00.TXT
IX-5	Drawings	6	-
IX-7	TOTAL	28	
	Accompanying items	paper document(s) attached	electronic file(s) attached
IX-8	Fee calculation sheet	✓	-
IX-17	PCT-EASY diskette	-	Diskette
IX-19	Figure of the drawings which should accompany the abstract	6	
IX-20	Language of filing of the international application	English	
X-1	Signature of applicant, agent or common representative		
X-1-1	Name	MCCALLUM RADEMEYER & FREIMOND	
X-1-2	Name of signatory	M.A.J. Rademeyer	
X-1-3	Capacity	Agent	

FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	05 JUN 2002
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application	
10-4	Date of timely receipt of the required corrections under PCT Article 11(2)	
10-5	International Searching Authority	ISA/EP
10-6	Transmittal of search copy delayed until search fee is paid	

FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by the International Bureau	
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PCT (ANNEX - FEE CALCULATION SHEET)

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(This sheet is not part of and does not count as a sheet of the international application)

0	For receiving Office use only		
0-1	International Application No.	PCT/ZA02/00096	
0-2	Date stamp of the receiving Office	05 JUN 2002	
0-4	Form - PCT/RO/101 (Annex) PCT Fee Calculation Sheet		
0-4-1	Prepared using	PCT-EASY Version 2.92 (updated 01.01.2002)	
0-9	Applicant's or agent's file reference	INT1056/MAJR	
2	Applicant	BILLITON SA LIMITED, et al.	
12	Calculation of prescribed fees	fee amount/multiplier	Total amounts (ZAR)
12-1	Transmittal fee T	⇒	500
12-2-1	Search fee S	⇒	7,570
12-2-2	International search to be carried out by	EP	
12-3	International fee		
	Basic fee		
	(first 30 sheets) b1	3,560	
12-4	Remaining sheets	0	
12-5	Additional amount (X)	80	
12-6	Total additional amount b2	0	
12-7	b1 + b2 = B	3,560	
12-8	Designation fees		
	Number of designations contained in international application	93	
12-9	Number of designation fees payable (maximum 5)	5	
12-10	Amount of designation fee (X)	770	
12-11	Total designation fees D	3,850	
12-12	PCT-EASY fee reduction R	-1,090	
12-13	Total International fee (B+D-R) I	⇒	6,320
12-14	Fee for priority document		
	Number of priority documents requested	1	
12-15	Fee per document (X)	200	
12-16	Total priority document fee P	⇒	200
12-17	TOTAL FEES PAYABLE (T+S+I+P)	⇒	14,590
12-19	Mode of payment	cheque	

VALIDATION LOG AND REMARKS

PCT (ANNEX - FEE CALCULATION SHEET)

INT1056/MAJR

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13-2-7	Validation messages Contents	Yellow! The power of attorney or a copy of the general power of attorney will need to be furnished unless all applicants sign the request form.
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SOLVENT EXTRACTION MIXTURE FOR THE
SEPARATION OF GROUPS OF BASE METALS

BACKGROUND OF THE INVENTION

This invention relates to a mixture of organic compounds suitable for the solvent extraction-based separation of base metals and associated impurities from weakly acidic sulphate solutions.

Hydrometallurgical methods to recover base metals from ores, concentrates or intermediates have increased in popularity due to the perceived reduced environmental impact in comparison with smelting operations. Their application is frequently hindered by the lack of suitable methods for the selective recovery of the metals of interest in a pure form.

Acidic sulphate solutions could be obtained by direct acid leaching of processing residues, ores or concentrates containing oxides and/or secondary sulphides of base metals. They could also be obtained by treating similar but more refractory materials by low pressure oxidation (Activox process), standard pressure oxidation or bioleaching of sulphides, or high temperature acid leaching of refractory oxide ores.

The resulting aqueous sulphate solution, which could also contain other anions such as chloride and nitrate, mostly contains the base metals Cu, Ni, Co, Zn, Cd and Pb, additional impurities such as Mn, Fe(II), Fe(III), and the alkaline earth metals Ca and Mg, their relative concentrations depending on the ore/intermediate being treated.

The removal of appreciable amounts of copper from such solutions can be effected by selective cementation with scrap iron or by solvent extraction (SX) with hydroxy-oxime based extractants (LIX-extractants).^(1,2) In both instances, the presence of ferric ions in the leach solution will affect the efficiency of the downstream recovery process and its efficient removal is highly recommended but not always readily achieved, not even with hydroxy-oxime based extractants.

Pregnant solutions obtained by leaching zinc oxide ores or roasted sulphide concentrates or direct bioleaching of sulphides, are traditionally treated by a

combination of neutralisation/precipitation and cementation to remove undesirable impurities such as Fe, Ni, Co, Cu, Cd and Pb before electrowinning (EW).⁽³⁻⁷⁾ This is normally associated with appreciable losses of zinc. More recently, SX has also been used as a means of purifying the primary leach liquor with the added advantage that the zinc content of the pregnant liquor can be increased to suit subsequent EW requirements.

The preferred extractant appears to be di-2-ethyl hexyl phosphoric acid (DEHPA) which is not very selective for zinc and tends to co-extract impurities such as Fe, Al, Pb, Cd and Ca if a raffinate with a low zinc content is required.^(8,9)

10 Treatment of nickel/cobalt pregnant solutions tends to be more complicated. The main impurities in such solutions are typically Fe, Mn, Ca, Mg, Cu and, to a lesser extent, Zn. The separation of nickel and cobalt can readily be effected with a SX reagent such as bis(2,4,4-triethylpentyl)-phosphinic acid (CYANEX 272), but this does not offer the opportunity of removing impurities as required for the subsequent EW process.⁽¹⁰⁻¹³⁾

15 Various strategies have been developed to effect the purification and separation required to obtain high purity products in the form of salts, oxides or metals.

In the more traditional downstream treatment procedure, the weakly acidic sulphate solution is treated with sulphide to selectively precipitate the base metals and effect removal of other dissolved impurities, mainly Mn, Ca, Mg and other alkaline earth or alkali metals.⁽¹³⁻¹⁵⁾ The main disadvantage of this option is that the precipitate needs to be redissolved by pressure oxidation before further purification and separation of cobalt and nickel can be considered.

25 In an alternative option, the base metals are precipitated as hydroxides by neutralising the solution with MgO or CaO.⁽¹⁶⁻²¹⁾ The main advantage of this procedure is that the base metals in the precipitate can be re-leached in ammonia, ammonium sulphate or ammonium carbonate solutions at atmospheric pressure. The main disadvantage, in comparison with sulphide precipitation, is that rejection of manganese and the alkaline earth metals is less efficient as they tend to coprecipitate with the base metals. They are, however, largely insoluble during re-leaching but the presence of manganese tends

to cause incomplete recovery of nickel and cobalt necessitating an additional strong acid leaching stage to prevent losses of these metals.

Further potential solutions are based on SX only, eventually after removal of Fe, Al and Cr by neutralisation/precipitation.

- 5 In one proposed option, base metals are selectively extracted from strongly acidic solutions with a di-thiophosphinic acid commercial extractant (CYANEX 301) leaving Ca, Mg and Mn in the raffinate. Subsequently, the base metals are stripped from the organic phase for further separation and purification.⁽²²⁾

- Other systems, under investigation or proposed, usually involve the use of a carboxylic acid (typically Versatic acid), a di-alkyl phosphoric acid (DEHPA) and CYANEX 272 in various configurations.^(10-12,21) In these instances, Versatic acid is mainly used to remove the majority of Mn, Ca and Mg without major losses of base metals, but does not offer any possibility of separating any of the base metals. It also has the disadvantage of high water solubility at the elevated pH required for effective nickel/cobalt recovery.

- Better rejection of the unwanted impurities, and especially calcium and manganese, can be obtained by adding a synergistic compound to the Versatic acid-containing extraction mixture with an associated reduced pH for effective nickel/cobalt extraction as an added advantage.⁽²³⁻²⁶⁾ As an alternative, a second extraction can be done on the acidic solution, obtained by stripping the loaded Versatic acid mixture, with a DEHPA based extraction mixture to remove further amounts of calcium and manganese with the added advantage of also removing Zn, Pb, Cd and Cu if present.^(26,27) However, the use of SX to remove trace amounts of impurities is usually not very cost effective. In addition, extreme care must be taken to avoid losses of nickel/cobalt during this step.

- 25 CYANEX 272 is typically used to separate cobalt and nickel, either before or after partly removing Ca, Mg and Mn impurities using Versatic acid mixtures. However, other base metals, if still present, are co-extracted and special techniques, such as selective stripping, are required to obtain an impurity-free solution suitable to produce a high purity product.

From the preceding observations it is clear that an extraction mixture capable of simplifying the procedure to obtain purified base metal sulphate solutions, suitable to be converted to high purity products, will be of great benefit to the industry as it will reduce the complexity of the processes and the associated costs.

5 OBJECT OF THE INVENTION

It is an object of the invention to provide a mixture of organic compounds which is suitable to be used as a solvent extractant to treat acidic sulphate solutions and which is capable of:

- a) selectively rejecting unwanted impurities including manganese, lead, alkaline earth metals, alkali metals and ammonium ions;
- b) selectively extracting groups of certain base metals by direct extraction or by differential stripping or by a combination of these, and
- c) selectively removing single base metals by direct extraction or by differential stripping.

15 SUMMARY OF THE INVENTION

The invention provides an organic solvent extraction mixture which includes:

- (a) a first extractant, which is a substituted imidazole (Diagram 1) or benzimidazole (Diagram 2):

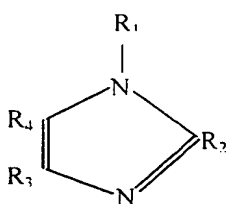


Diagram 1

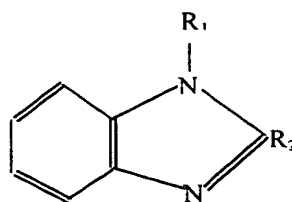


Diagram 2

and wherein the substituents are:

- R_1 = an organic group which:
 - is branched or unbranched;
 - is saturated or partly unsaturated;

- contains aromatic groups or not;
- is with or without other functional groups; or
- is an esterified fatty acid group;

and wherein R_1 may have between 2 and 20 carbon atoms

and preferably has between 6 and 15 carbon atoms;

- R_2 = hydrogen or a methyl group, preferably hydrogen;
- R_3 = hydrogen or a short chain organic group with 1 or 2 carbon atoms, preferably hydrogen or a methyl group; and
- R_4 = hydrogen or a short chain organic group with 1 or 2 carbon atoms, preferably hydrogen or a methyl group;

b) a non-selective strongly acidic cation second extractant, such as a sulphonic acid ($R-SO_3H$), to facilitate phase transfer of base metal ions from aqueous weakly acidic sulphate solution into the organic phase, and wherein R is an aliphatic group, either saturated or unsaturated and branched or unbranched, an aromatic organic group or a mixed group consisting of aliphatic and aromatic parts, with between 3 and 40 carbon atoms, preferably with between 8 and 30 carbon atoms;

c) a modifier to improve the characteristics of the organic phase with respect to metal complex solubility to avoid third phase formation, completeness and ease of stripping, viscosity and phase disengagement; and

d) a diluent, which is selected from non-specific aliphatic or aromatic or partly aliphatic, partly aromatic mixtures of unspecified composition with a moderate boiling point range and a suitable flash point, such as Kerosene, Shellsol (various grades), Escald (various grades), Solvesso and similar products.

The concentration of the first extractant can be between 0.01 and 1.50 Molar, depending on the capacity required and preferably is between 0.25 and 1.50 Molar for commercial applications.

Typical examples of the second extractant include: di-nonyl naphthalene sulphonic acid (DNNS), di-dodecyl naphthalene sulphonic acid, di-n-octyl methyl sulphonic acid and

alkyl-substituted benzene sulphonic acid which are commercially available or easy to synthesise.

5 The concentration of this second extractant may be between 0.001 to 1.0 Molar sulphonic acid, preferably between 0.05 to 0.6 Molar, the optimum being 10% to 25% of the extractant concentration and 40% to 100% of the maximum metal molarity in the organic phase.

The modifier is preferably characterized by the presence of a sterically available oxygen or nitrogen atom with lone pairs of electrons as in phenols, alcohols, esters of inorganic and organic acids, ketones, aldehydes, ethers, organic acids, amines and amides.

10 The modifier may be added at a concentration of from 20% to 75% and preferably at a concentration of 30% to 70% of the total mixture.

The diluent can be added at a concentration sufficient to make up a total of 100% for the mixture.

15 Extractions can be carried out in the temperature range between 10°C and 70°C and preferably between ambient and 45°C.

The aqueous pregnant feed solution to be treated can also contain moderate amounts of non-complexing cations, such as nitrate, chlorate or perchlorate, and also appreciable amounts of chloride up to a concentration of 3 Molar.

20 Extractions can be carried out at an aqueous pH between 0.0 and 6.0, the preferred pH depending on the objective of the extraction process. This value can readily be estimated from the results given in the Examples by those skilled in the art of solvent extraction-based separations.

25 Stripping of the organic phase can readily be effected with a dilute aqueous sulphuric acid solution at a concentration equal to or slightly higher than the change in the metal concentration in the aqueous strip solution during the stripping process.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further described by way of examples with reference to the accompanying drawings in which:

Figures 1, 2 and 3 are flow diagrams of different standard solvent extraction processes, and

Figures 4 to 11 are curves of extraction efficiency as a function of pH for different extractants, with Figures 6 to 11 relating to extractants according to the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

The invention can be applied using any standard solvent extraction apparatus consisting of an extraction section and a single or double stripping action, with an optional washing or scrubbing section in between, and suitable to simulate standard solvent extraction processes as shown in any of the flow sheets in Figures 1 to 3 respectively.

The flow sheets shown in Figures 1 to 3 are largely self-explanatory and are known in the art. They are therefore not described in detail hereinafter.

In the following Examples a comparison is made of the results obtained by using organic solvent extractant mixtures according to the invention and the results obtained using other extractants. Examples 1 and 2 relate to the use of organic extraction mixtures which do not fall inside the scope of the invention while the remaining Examples illustrate results obtained using organic extraction mixtures which fall within the scope of the invention.

Example 1

Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, were contacted with an organic mixture containing 0.02 Molar DNNS in an iso-decanol (30%) – Shellsol A mixture at an A:O ratio of 1:1. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the %

extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction. The results in Figure 4 indicate that DNNS is a non-selective extractant for divalent cations with optimum extraction in the pH range 1.00 to 3.0.

Example 2

Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, were contacted with an organic mixture containing 0.1 Molar 1-decylimidazole (DIMZ) in an iso-decanol (70%) – Shellsol A mixture at an A:O ratio of 1:1. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction. The results in Figure 5 indicate that, with DIMZ only present, only copper is extracted and only to a limited extent even in the presence of a large excess of extractant.

Example 3

Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, were contacted with an organic mixture containing 0.1 Molar 1-decylimidazole (DIMZ) and 0.007 Molar DNNS in an iso-decanol (70%) – Shellsol A mixture at an A:O ratio of 1:1. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

The results in Figure 6 indicate that, with both DIMZ and DNNS present, copper is extracted at a pH of ~ 3.0 and the other base metals at a pH around 4.0. Mg and Mn are hardly extracted even at pH 6.0. From this it is evident that manganese and magnesium

could be removed from a mixed sulphate solution according to the flow sheet given in Figure 1. Similarly, copper could be removed according to the flow sheet given in Figure 3.

Example 4

5 Aqueous solutions of individual metal sulphate salts, at 0.025 Molar, were contacted with an organic mixture containing 1.5 Molar 1-decylimidazole (DIMZ) and 0.15 Molar DNNS in iso-decanol (no other diluent) at an A:O ratio of 1:1. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was
10 determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction. The results in Figure 7 indicate that, with both DIMZ and DNNS present at high concentration, copper is extracted at a pH of ~ 2.5 and the other base metals at a
15 pH around 3.5, which are about 0.5 pH units lower than the values found in Example 3. Mg, Ca, Pb and Mn are hardly extracted even at pH 5.0.

From this it is evident that manganese, lead, calcium and magnesium could be removed from a mixed sulphate solution according to the flowsheet given in Figure 1. Similarly, copper could be removed according to the flowsheet given in Figure 3. The difference in
20 the extraction pH for nickel and cobalt is small, but large enough to allow selective extraction of nickel from cobalt, if the concentration of the latter is relatively small, according to the flowsheet given in Figure 2.

Example 5

25 An aqueous solution of metal sulphates, obtained by bioleaching a nickel sulphide concentrate, after removal of dissolved iron, containing Ni (1.27 g/l), Cu (3.94 ppm), Co (17.3 ppm), Mg (118 ppm), Mn (2.26 ppm) and Zn (0.66 ppm) was contacted with an organic mixture containing 1.5 Molar 1-decylimidazole (DIMZ) and 0.15 Molar DNNS in iso-decanol (70%). The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal

concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction. The results in Figure 8 indicate that extraction of the metals present in the mixture is very similar to their extraction from single metal sulphate solutions (Example 4, Figure 7). However, the extraction of zinc and cadmium, which are only present at very low concentrations, is shifted to higher pH values to coincide with the extraction of cobalt. Mg, Mn, Ca and Pb are hardly extracted even at pH 4.0, when extraction of the other metals is virtually complete.

From this it is evident that manganese, lead, calcium and magnesium could be removed from a mixed sulphate solution according to the flowsheet given in Figure 1. Similarly, copper could be removed from other base metals according to the flowsheet given in Figure 3. The difference in the extraction pH for nickel and cobalt, cadmium or zinc is small, but large enough to allow selective extraction of nickel from these elements by including an effective scrub section according to the flowsheet given in Figure 2.

Example 6

An aqueous solution of nickel sulphate, at 0.001 Molar, was contacted with an organic mixture containing 0.1 Molar 1-decylimidazole (DIMZ) and different concentrations of DNNS in an iso-decanol (70%) – Shellsol A mixture at an A:O ratio of 1:1. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

The results in Figure 9 indicate that, without DNNS present, nickel is hardly extracted even at a pH of 4.9. Effective nickel extraction is already achieved at a DNNS concentration of 0.002 Molar. Nickel extraction improves only marginally with a further increase in DNNS concentration, although the extraction curves are steeper, which is an advantage when separating metals with similar extractability. A large excess of DNNS,

up to 0.020 Molar for 0.001 Molar metal concentration, does not affect the extraction adversely.

Example 7

Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, were contacted with an organic mixture containing 0.1 Molar N-substituted imidazole (N-octylimidazole, N-decylimidazole and N-duodecylimidazole) and 0.010 Molar DNNS in an iso-decanol (70%) – Shellsol A mixture at an A:O ratio of 1:1. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

The results in Figures 10a and 10b, together with those from Example 3 (Figure 6), indicate that the extraction of the various metals is hardly affected by the substituent group, although the extraction is slightly weaker with N-duodecyl imidazole.

Example 8

Aqueous solutions of individual metal sulphate salts, at 0.001 Molar, containing also chloride at a concentration of 0.77 Molar, were contacted with an organic mixture containing 0.1 Molar 1-decylimidazole (DIMZ) and 0.010 Molar DNNS in an iso-decanol (70%) – Shellsol A mixture at an A:O ratio of 1:1. The pH of the aqueous phase was adjusted to the target value using either aqueous sulphuric acid or sodium hydroxide solutions. The residual metal concentration in the aqueous phase was determined to calculate the % extraction. Occasionally, the organic phase was contacted with aqueous 1.0 Molar sulphuric acid to strip the metals. The recovered metal in the strip solution was then also determined to calculate and verify the % extraction.

The results in Figure 11, together with those from Example 3 (Figure 6), indicate that the extraction of zinc is strongly enhanced by the presence of chloride in the aqueous phase. The extraction of copper and cobalt is only slightly enhanced and that of nickel is

not affected at all. The extractability of magnesium and manganese remains low and is even weaker if chloride is present.

The results show that the presence of chloride, either due to circumstances or by design, is advantageous for the selective separation of certain groups of base metals
5 such as Cu/Zn and Ni/Co from each other and each from the non-extractable impurities.

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CLAIMS

An organic solvent extraction mixture which includes:

a first extractant, which is a substituted imidazole (Diagram 1) or benzimidazole (Diagram 2):

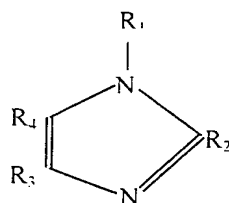


Diagram 1

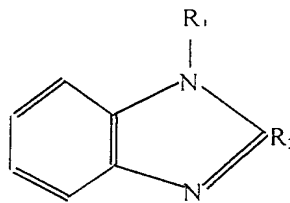


Diagram 2

and wherein

- R_1 = an organic group which has between 2 and 20 carbon atoms;
- R_2 = hydrogen or a methyl group;
- R_3 = hydrogen or a short chain organic group with 1 or 2 carbon atoms; and
- R_4 = hydrogen or a short chain organic group with 1 or 2 carbon atoms;

- a) a non-selective strongly acidic cation second extractant;
- b) a modifier; and
- c) a diluent.

2. A mixture according to claim 1 wherein R_1 has between 6 and 15 carbon atoms.

3. A mixture according to claim 1 or 2 wherein the concentration of the first extractant is between 0.01 and 1.50 Molar.

4. A mixture according to any one of claims 1 to 3 wherein the second extractant is a sulphonic acid ($R-SO_3H$) and R is selected from an aliphatic group, an aromatic organic group or a mixed group consisting of aliphatic and aromatic parts, with between 3 and 40 carbon atoms.

5. A mixture according to any one of claims 1 to 4 wherein the second extractant is selected from di-nonyl naphthalene sulphonic acid (DNNS), di-dodecyl naphthalene

sulphonic acid, di-n-octyl methyl sulphonic acid and alkyl-substituted benzene sulphonic acid.

6. A mixture according to claim 4 or 5 wherein the concentration of the second extractant is between 0.001 to 1.0 Molar sulphonic acid.

7. A mixture according to any one of claims 1 to 6 wherein the modifier is characterized by the presence of a sterically available oxygen or nitrogen atom with lone pairs of electrons.

8. A mixture according to any one of claims 1 to 7 wherein the concentration of the modifier is between 20% to 75% of the mixture.

9. A mixture according to any one of claims 1 to 8 wherein the diluent is selected from aliphatic, aromatic or aliphatic aromatic mixtures.

10. Use of the extractant mixture of any one of claims 1 to 9 which is carried out a temperature in a range between 10°C and 70°C and at a pH between 0 and 6.0.

11. Use according to claim 10 for the treatment of an aqueous pregnant feed solution.

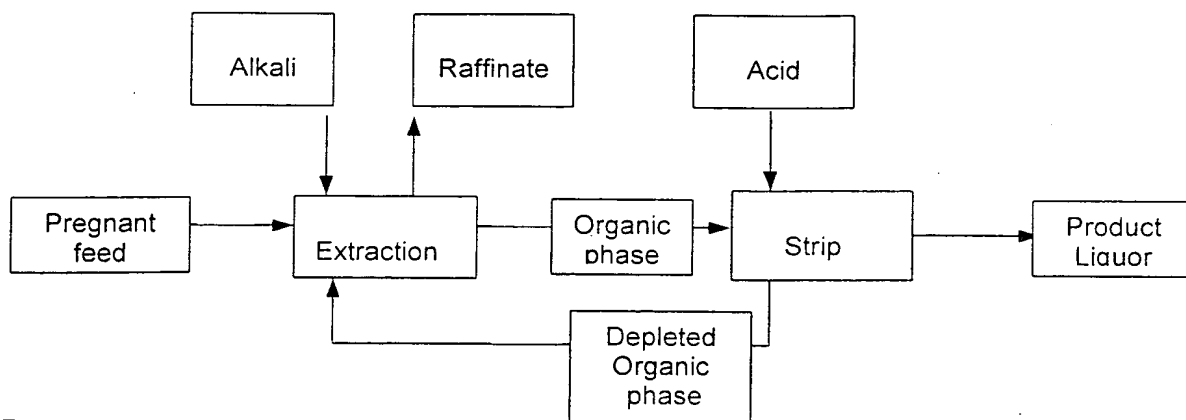


Figure 1: Basic solvent extraction flow sheet

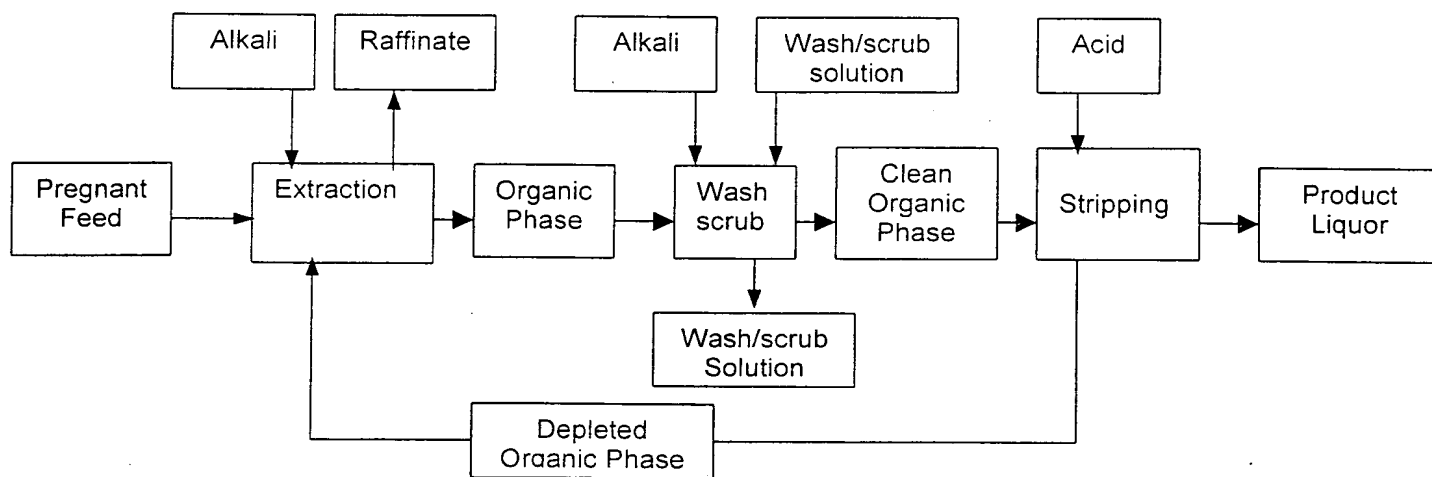


Figure 2: Solvent extraction flow sheet with wash/scrub section

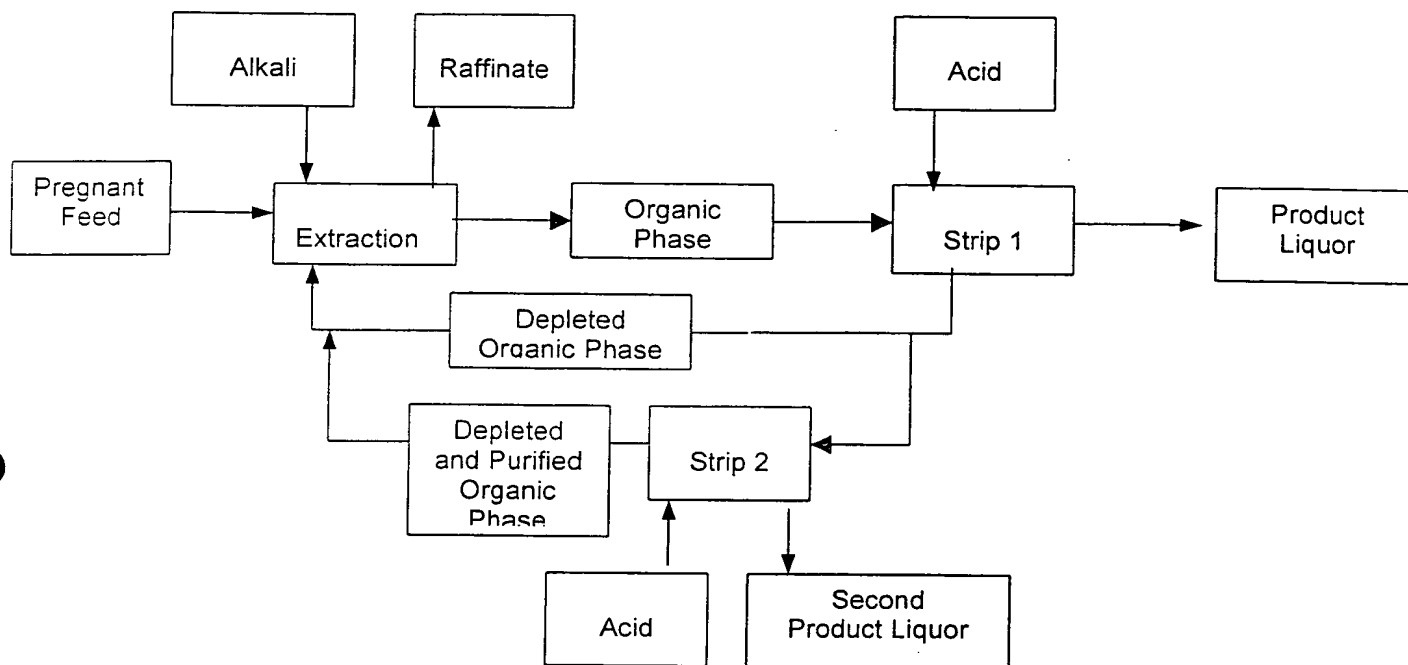


Figure 3: Solvent extraction flow sheet with second strip stage (differential stripping)

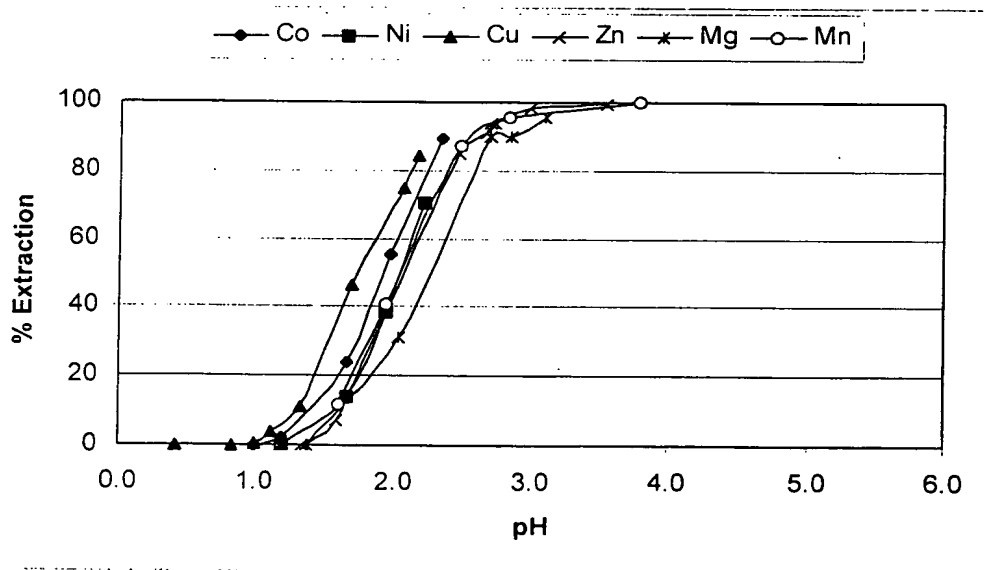


Figure 4: Extraction of individual metal ions with DNNS

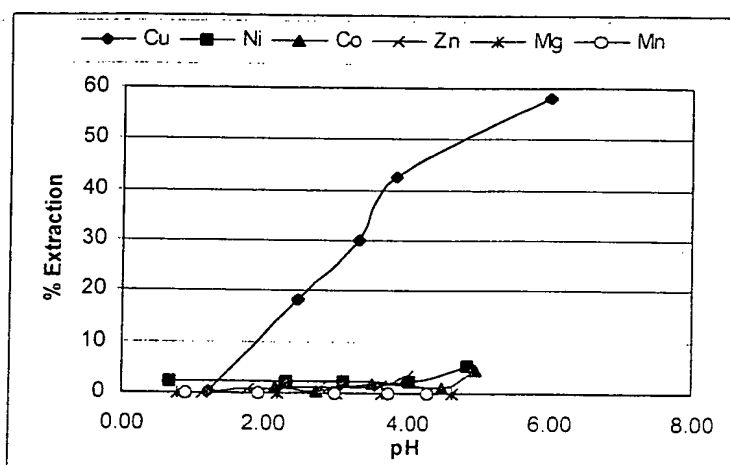


Figure 5: Extraction of individual metals in the absence of DNNS

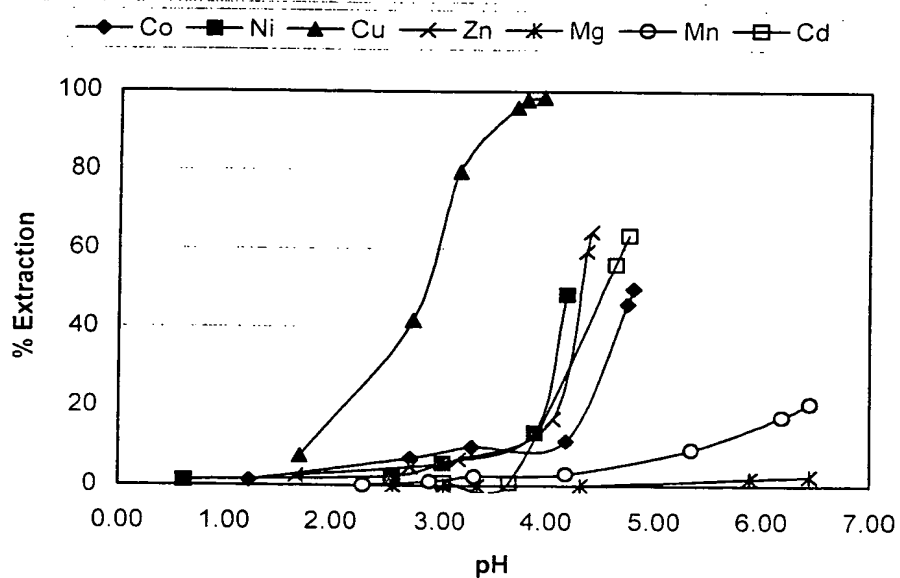


Figure 6: Extraction of individual metals with a mixture of DIMZ and DNNS (low concentration)

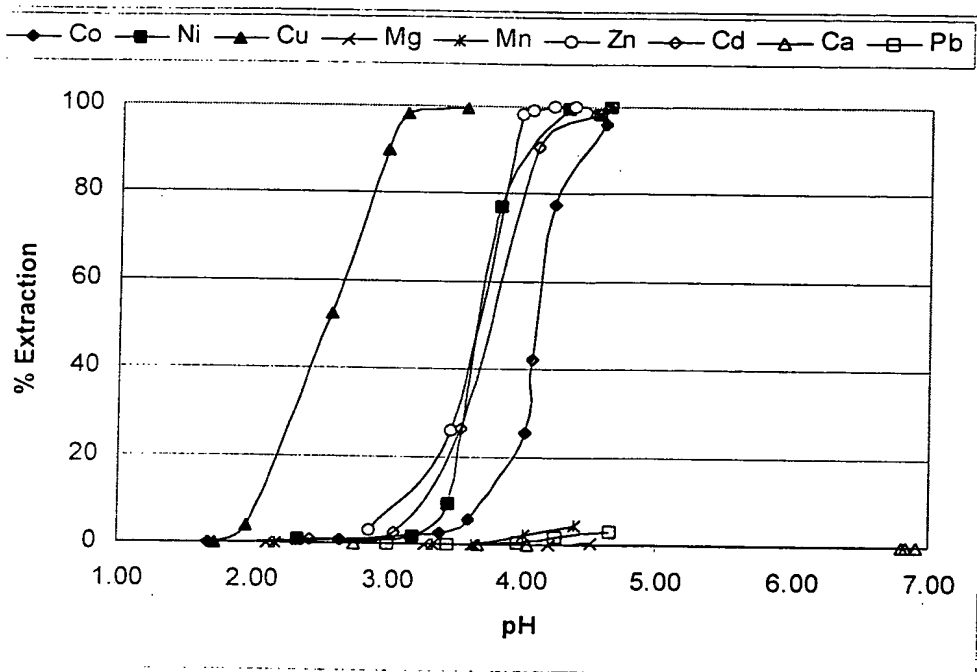


Figure 7: Extraction of individual metals with a mixture of DIMZ and DNNS (high concentration)

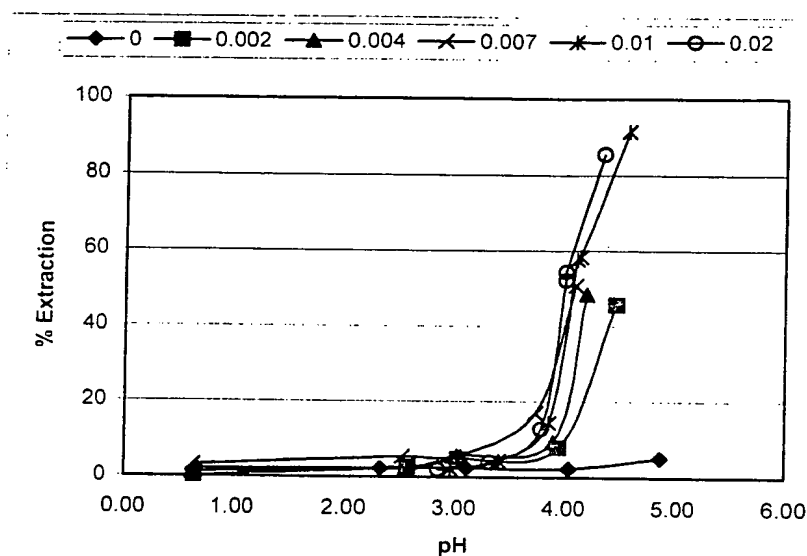


Figure 9: Extraction of nickel by DIMZ; influence of DNNS concentration

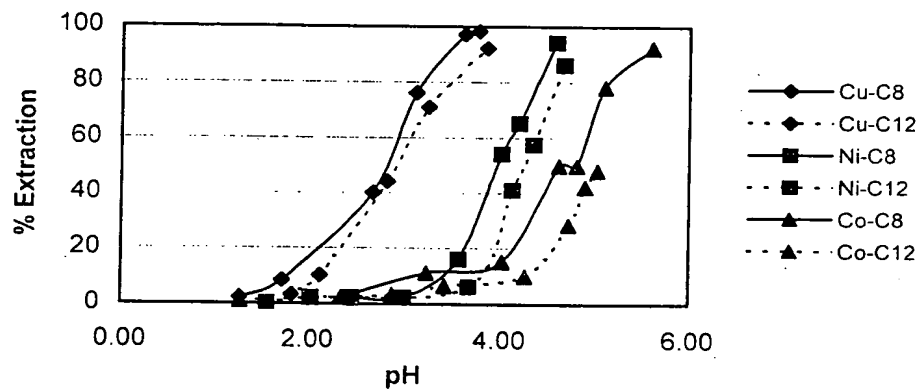


Figure 10a: Effect of substituent on metal extraction (C8=octyl; C12=duodecyl; Cu, Ni & Co)

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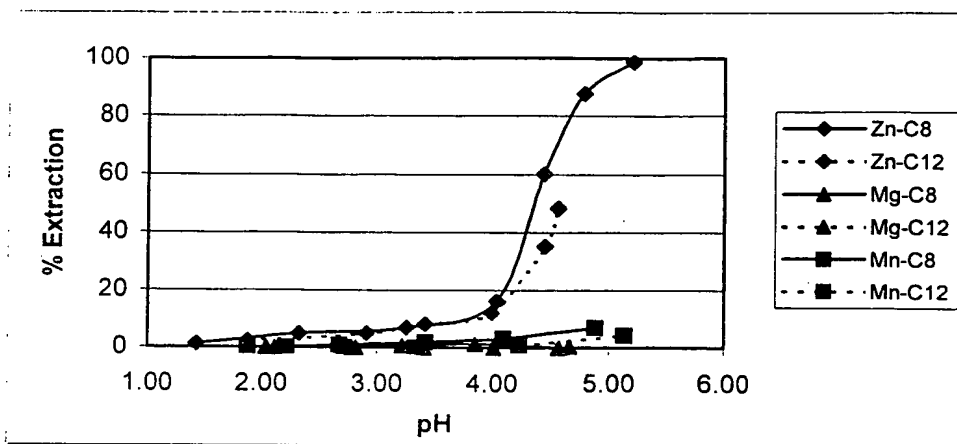


Figure 10b: Effect of substituent on metal extraction (C8=octyl; C12=duodecyl; Zn, Mg & Mn)

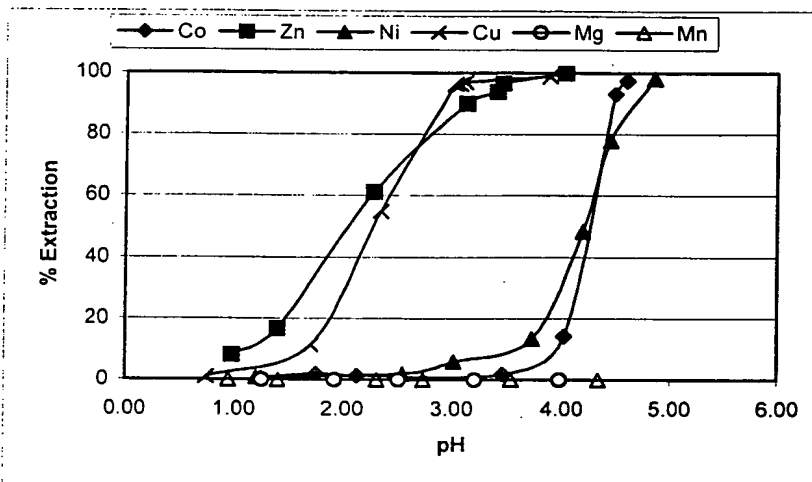


Figure 11: Extraction of metal ions with DIMZ/DNNS in the presence of 0.77 Molar chloride